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Influence of Uncompensated Solution Resistance

Upon the Evaluation of Rate Constants

for Rapid Electrochemical Reactions

by

David Milner and Michael J. Weaver
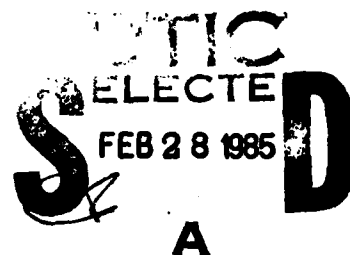
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INFLUENCE OF UNCOMPENSATED SOLUTION RESISTANCE UPON THE EVALUATION OF RATE CONSTANTS FOR RAPID ELECTROCHEMICAL REACTIONS

Apparent Observed rate Constants

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Standard rate Constants

We have recently outlined an experimental method whereby the reliability of observed standard rate constants for outer-sphere electrochemical reactions, k_{ob}^s, evaluated using a given technique and set of experimental conditions can be tested in a direct manner. This entails monitoring the response of the "apparent observed" values of k_{ob}^s, $k_{ob}^s(app)$, to systematic alterations of the double-layer structure caused by the addition of small concentrations of strongly specifically adsorbing anions. This procedure enables k_{ob}^s for the test reaction to readily be "tuned" over a wide range. These apparent rate variations, expressed as $\Delta \log k_{ob}(app)$, are compared with those observed under the same conditions for a structurally similar, yet irreversible "calibration" reaction having rate constants in the range ca. 10^{-4} to 10^{-2} cm/sec, where they can be evaluated reliably using straightforward d.c. methods. This comparison enables the extent of departure of $k_{ob}^s(app)$ from the corresponding "true" rate constants, $k_{ob}^s(true)$, for values that approach the suspected measurement limit to be obtained, provided that the data set also includes sufficiently small values of $k_{ob}^s(app)$ such that $k_{ob}^s(app) \simeq k_{ob}^s(true)$.

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true rate Constants

[†] This "apparent observed" rate constant should not be confused with the experimental rate constants, that we have often labelled "k_{app}", determined for slower electrode reactions for which there is little or no uncertainty associated with their evaluation. The latter apparent rate constants are usually labelled as such to distinguish them from "double-layer corrected" quantities where the influence of electrostatic work terms has been removed by recourse to theoretical treatments, most commonly the coupled Gouy-Chapman-Stern-Frumkin model.[2]

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This procedure was applied to the kinetics of $Ru(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_4(OH_2)_2^{3+/2+}$ at the mercury-aqueous interface as evaluated using a.c. polarography.[1] Although $k_{ob}^s(app) \approx k_{ob}^s(true)$ when $k_{ob}^s \leq 1$ cm sec^{-1}, for faster rate constants the values of $k_{ob}^s(app)$ become progressively smaller than $k_{ob}^s(true)$. In the present communication we present evidence derived from simulated a.c. polarographic responses that indicates that the major contributor to this measurement limit is associated with residual uncompensated solution resistance. A simple procedure is formulated by which the presence of the effect can be diagnosed and the magnitude of the correction to $k_{ob}^s(app)$ assessed.

Results and Discussion

As is conventional, the procedure employed for the a.c. polarographic measurements in ref. 1 involved using a potentiostat (PAR 173/179) featuring positive-feedback iR compensation.[3,4] The level of compensation was adjusted so that there was a minimal amount of solution resistance, R_s, that remained uncompensated, R_{us}. This corresponds to a compensation level just below that for which potentiostat oscillation occurs. The in-phase and quadrature components of the a.c. current measured in the absence of the reactant were subtracted from those measured in its presence ("linear background subtraction"), the differences used to obtain values of $k_{ob}^s(app)$ from plots of cot ϕ (where ϕ is the phase angle of the current) against the square root of the applied a.c. frequency.[5] This common procedure is anticipated to correct for the double-layer charging current, as well as for R_s. However, the electronic resistance compensation found on most commercial potentiostats will seldom correct entirely for the solution resistance and will usually leave values of R_{us} that are small and positive. This will inevitably yield some error in the derived rate constant using the above analysis procedure since this assumes that $R_{us} = 0$.[5,6]

The relations describing the a.c. polarographic response, including the effects of R_{us} and the double-layer capacitance, C_{dl}, as well as the usual contribution from the charge-transfer impedance,[5] can readily be derived from the usual equivalent circuit due originally to Randles.[7] We have utilized such relations to obtain simulated a.c. polarograms associated with a series of standard rate constants, k_{ob}^s(true), for various trial values of R_{us} and C_{dl}. The resulting polarograms were then analyzed in the manner described above for the experimental data, thereby yielding simulated values of k_{ob}^s(app).

These simulations produce plots of k_{obb}^s(app) versus k_{ob}^s(true) that are strikingly similar to those given in ref. 1. Figure 1 contains experimental values of log k_{ob}^s(app) plotted versus log k_{ob}^s(true) for $Ru(NH_3)_6^{3+/2+}$ at the mercury-aqueous interface (open circles, taken from ref. 1), along with a corresponding plot (solid curve) extracted from the simulated polarograms. The latter was obtained using a value of C_{dl}, 0.4 µF, that is appropriate for the experimental conditions in ref. 1 (0.1 $\underline{M}$ KPF_6; electrode area = 0.02 cm^2); a value of R_{us}, 3 ohms, was chosen so to yield the best fit to the experimental points.

This R_{us} value is physically quite reasonable, being much smaller than the experimental value of R_s, 370 ohms, determined for the conditions in ref. 1 by a.c. impedance measurements without iR compensation and in the absence of the reactant. Indeed, similar values of R_{us} (3 ± 1 ohms) were determined for the potentiostat circuitry employed in ref. 1 from measurements of the in-phase and quadrature currents, I_I and I_Q respectively, for an RC dummy cell. This was employed rather than the actual electrochemical cell containing only supporting electrolyte since the latter yielded inconveniently small values of I_I. The potentiostat was connected to a 370 ohm resistor in series with a 0.4 µF capacitor (so to mimic the actual cell conditions) and

the iR compensation optimised. The capacitance was then increased suffi-
ciently (5 to 20 fold) so to yield measurable values of I_I at 500 Hz; R_{us} then
was determined from $R_{us} = EI_I/(I_Q^2 + I_I^2)$, where E is the amplitude of the a.c.
potential. (The presence of an additional resistor between the reference
and counter leads of the potentiostat had little effect on the results, at
least at the frequencies employed for the kinetic measurements, 40-1400 Hz).

Figure 2 contains further plots of log k_{ob}^s(app) against log k_{ob}^s(true)
extracted from simulated polarograms for representative values of C_{dl} and
R_{us}. It is seen that the effect of increasing the uncompensated resistance
is always to increase the error involved in the conventional analysis, as
expressed by the discrepancy between k_{ob}^s(app) and k_{ob}^s(true). The effect of
increasing C_{dl} for a given value of R_{us} is noticeably milder. Also worthy
of note is the coincidence of k_{ob}^s(app) with k_{ob}^s(true) when $R_{us} = 0$, even when
$D_{dl} \neq 0$ (Fig. 2, curve 1). This is because the effect of the latter in the
absence of the former is entirely accounted for by the "linear background
substraction" procedure described above. Clearly evident in Fig. 2, however,
is the presence of an upper limit to the rate constant that can be determined
if the effect of the solution resistance is not eliminated entirely. Even
though the actual rate constant may be much larger than that which can be
evaluated by using a.c. impedance (or other electrochemical perturbation tech-
niques), the determined rate constant will never exceed a value determined by
the experimental conditions. The experimental data analyzed by the usual
procedure given no obvious indication that the actual rate constant differs
from the measured value.

Rigorous, albeit relatively tedious, procedures for subtracting out
the contributions of the solution resistance and double-layer capacitance
to the a.c. polarographic response have been described.[5-8] These methods
involve a separate, direct measurement of R_s and C_{dl} rather than electronic

compensation, and are in principle capable of circumventing the limitations of the simplified treatment employing positive-feedback iR compensation if R_s is known accurately. However, similarly small errors in the direct measurement of R_s as those in its electronic compensation may well provide the major practical limitation to the magnitude of k_{ob}^s that can be reliably evaluated even using these sophisticated analyses.

The present considerations suggest a straightforward means of correcting the k_{ob}^s(app) values determined using the conventional analysis for nonzero values of R_{us}. Provided that R_{us} can be determined at least approximately for the particular instrument and experimental conditions employed, the k_{ob}^s(true) value can simply be read off from a simulated plot of k_{ob}^s(app) versus k_{ob}^s(true) generated for the appropriate value of R_{us} along with C_{dl} and the reactant diffusion coefficient. This procedure serves to diagnose as well as minimise the deleterious effects of solution resistance upon the accuracy of the derived electrochemical rate parameters. Although the present analysis is concerned only with a.c. polarography, similar treatments can readily be formulated to account for solution resistance effects upon rate constants evaluated using other perturbation techniques, such as cyclic voltammetry.

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<u>Figure Captions</u>

<u>Figure 1</u>

Comparison of plot of measured standard rate constants, k_{ob}^s(app), for $Ru(NH_3)_6^{3+/2+}$ at mercury-aqueous interface against corresponding "true" values, k_{ob}^s(true) (open circles, from ref. 1), with plot obtained from simulated a.c. polarograms with uncompensated resistance R_{us} = 3 ohms (solid line). Other simulation conditions corresponded to experimental conditions as in ref. 1: electrode area = 0.02 cm^2, reactant concentration = 1 m$\underline{M}$; diffusion coefficient = 8 x 10^{-6} cm^{-2} sec^{-1}; C_{dl} = 0.4 μF, a.c. frequencies 100-1100 Hz.

<u>Figure 2</u>

Evaluation of the effects of varying R_{us} and C_{dl} upon differences between k_{ob}^s(app) and k_{ob}^s(true). Simulation conditions as in Figure 1, except R_{us} and C_{dl} as follows: Curve 1 (straight line), R_{us} = 0 ohms; curve 2, R_{us} = 1 ohm, C_{dl} = 0.4 μF; curve 3, R_{us} = 2 ohm, C_{dl} = 0.2 μF; curve 4, R_{us} = 2 ohm, C_{dl} = 0.4 μF; curve 5, R_{us} = 2 ohm, C_{dl} = 0.8 μF; curve 6, R_{us} = 4 ohms, C_{dl} = 0.4 μF.
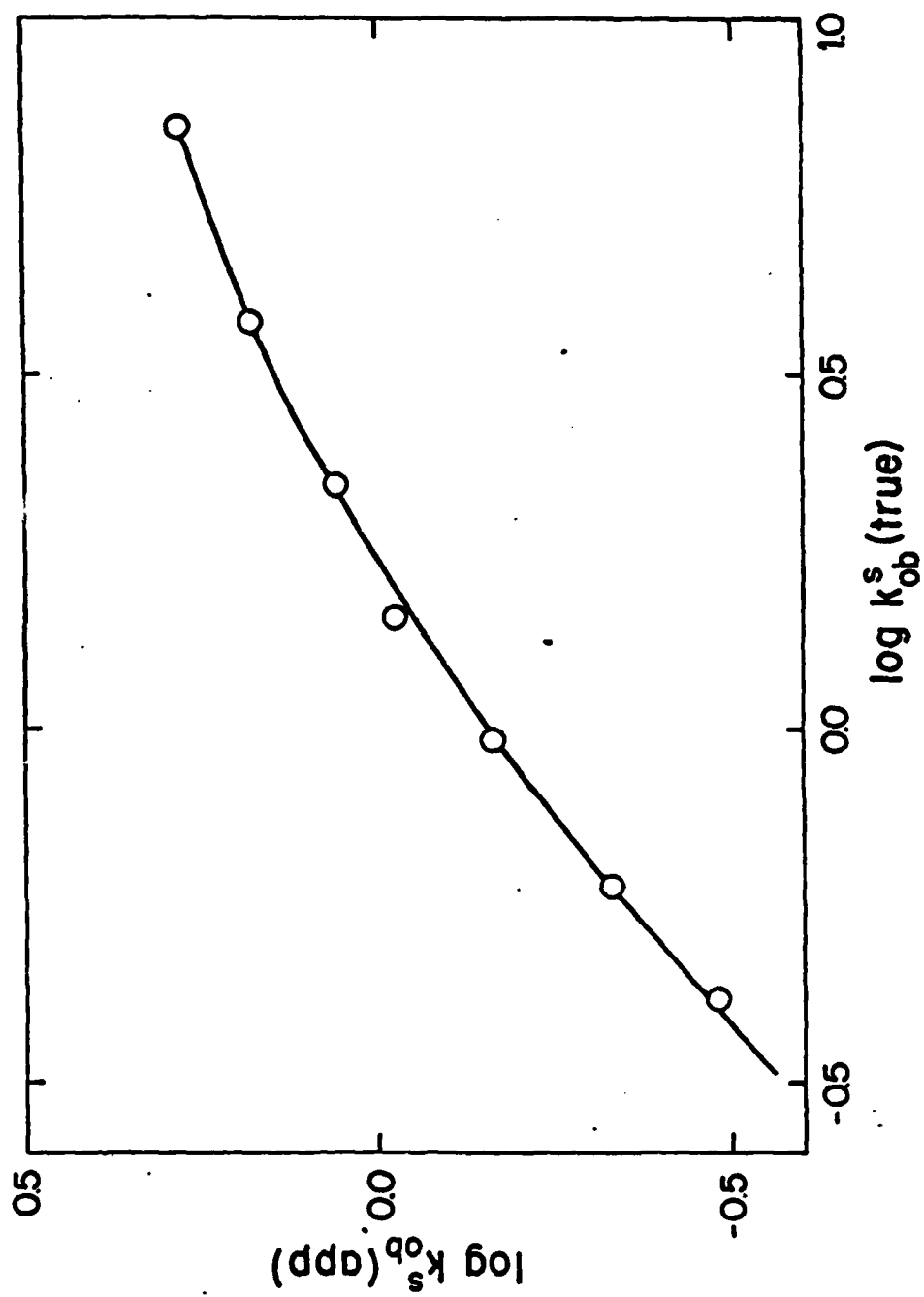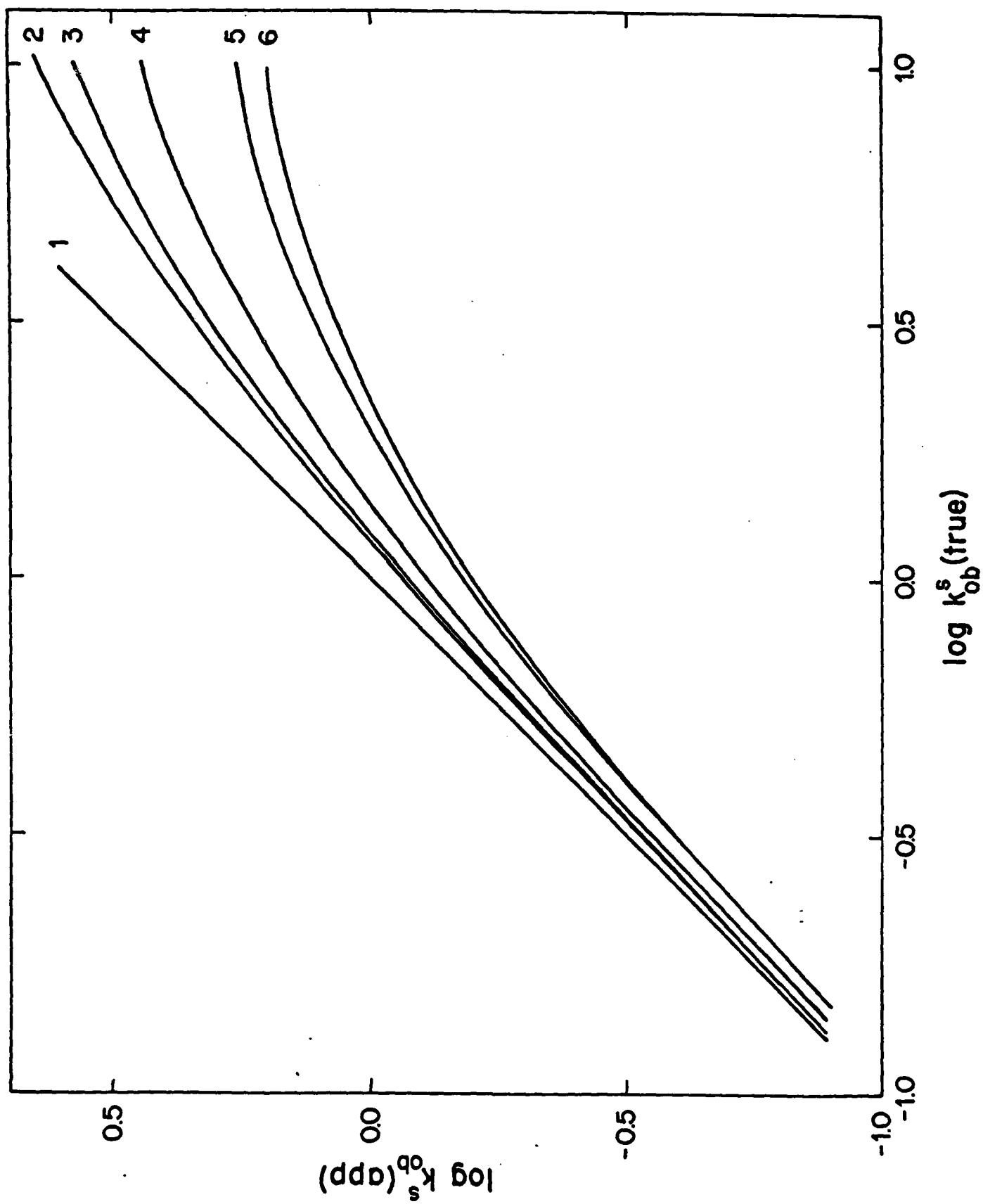
Fig 1

Fig. 2

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